Comparing Heavy Metals Accumulation Potential in Natural Vegetation and Soil Adjoining Wastewater Canal

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Summary: Heavy metal (HM) pollution of waters, soils and vegetation is a major ecological problem that needs to be investigated. The present study involved the collection of soil samples and natural vegetations (*Tribilas terristris, Lepia nodiflora, Amaranthus viridis, Heliotropium euoropeum, Coronopis didymus, Cynodon ductylon*, *Chenopodium murale* and *Eclipta alba*) from the vicinity of wastewater canal and subsequent analysis for their HM concentrations. Results showed that HM concentrations varied within the species of vegetation and type of metal analyzed. The order of vegetation for metal concentrations was *A. viridis* > *E. alba* > *H. euoropeum* > *L. nodiflora* > *C. murale* > *C. didymus* > *C. ductylon* > *T. terristris*. Metals prevailed in plants in the decreasing order of Fe > Mn > Zn > Pb > Cr > Cu > Cd, irrespective of the vegetation. Metal prevalence in soils was in the order of Fe > Mn > Cd > Cr > Pb > Zn > Cu. Samples near canal were found with higher level of Mn, Pb and Zn as compared to soil away from canal water. Distant sampling gave higher accumulation of Cd, Cr, Cu and Fe as compared to the soil nearby wastewater. The analyzed species of HM in the soils and plants may indicate the variability of their composition in wastewater.

Introduction

Heavy metal accumulation in plant and soil from natural and artificial sources poses significant threats to ecological phenomena [1-6] that need to be addressed. The primary sources of elements from the environment to plants are: air, water and the soil [7]. Among the elements, the most important to consider in terms of food chain contamination are As, Cd, Hg and Pb. Simultaneously, some micronutrients (e.g. Cu, Cr, Ni, Zn) may be toxic to both plants and animals at high concentrations [8]. Plants are important components of ecosystems as they transfer elements from abiotic into biotic environment. Phytoremediation involves the use of plants to remove, transfer, stabilize and/or degrade contaminants in soil, sediment and water [9]. Phytostabilization uses certain plant species to immobilize contaminants in soil, through absorption and accumulation by roots, adsorption onto roots or precipitation within the root zone and physical stabilization of soils. It reduces the mobility of the contaminants and prevents further movement of the contaminant into groundwater or the air and reduces the bioavailability for entry into the food chain. Phytoremediation is less expensive process for wastewaters than other methods [10]. The ideal phytoremediator is a species that possesses large biomass, grows quickly, has an extensive root system and must be easily cultivated and harvested [11]. Heavy metals are ubiquitous environmental contaminants in industrialized societies. Soil pollution by metals differs from air or water pollution, because heavy metals persist in soil much longer than in other compartments of the biosphere [10]. Over recent decades, the annual worldwide release of heavy metals reached 22,000 t (metric ton) for cadmium, 939,000 t for copper, 783,000 t for lead and 1,350,000 t for zinc [12]. Increasing heavy metal accumulation at critical levels in living organisms from contaminated environment may have morbidity and mortality effects. Toxic heavy metals cause DNA damage and their carcinogenic effects in animals and humans are probably caused by their mutagenic ability [13, 14]. Exposure to high levels of these metals has been linked to adverse effects on human health and wildlife. Metal-contaminated soil can be remediated by chemical, physical or biological techniques [15]. Chemical and physical treatments irreversibly affect soil properties, destroy biodiversity and may render the soil useless as a medium for plant growth. These remediation methods can be costly. The adverse effects of waste waters on soils and crops have been researched intensively [16] But studies on the potential uptake of heavy metal in natural vegetations and soils nearby wastewater channels are scanty and have information gaps. Therefore, the objectives of this experiment were: 1) to investigate the horizontal metal transfer from wastewater stream to adjoining soil and 2) to

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compare the potential of natural vegetation (collected around a wastewater canal) to accumulate heavy metals.

Results and Discussion

Soil Analysis

Studying the impact of wastewaters on soils is important since soil is a medium to support plant growth and modulate water, nutrients and pollutants transport in the terrestrial environment. Soil analysis showed that wastewater canal appeared to regulate the form of heavy metal in the soil system (Fig. 1).

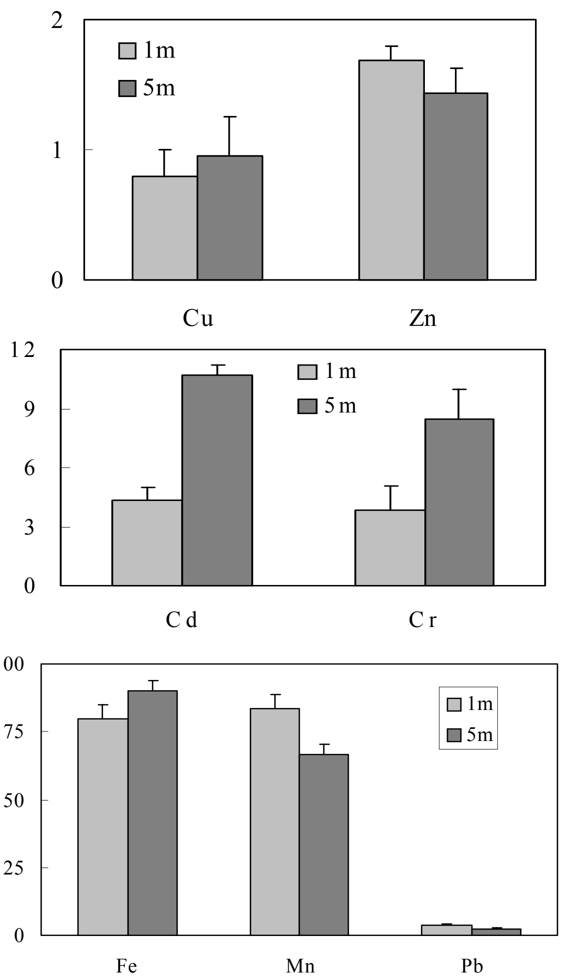

Fig. 1: Concentrations of heavy metals in soil samples (mg kg^{-1}) collected at distance of 1 m and 5 m around wastewater canal.

Naureen *et al.* [17] reported the concentrations of heavy metals in canal wastewater above the permissible limits for irrigation use (Table-1). Soil samples collected randomly near canal were significantly different for metal concentrations. In soil, the metal concentrations differed in the order of Fe > Mn > Cd > Cr > Pb > Zn > Cu. These metal species in soil may also reflect the variability of their composition in the canal wastewater. The concentrations trend of metals with respect to the distance from the canal also varied. The average concentrations of Mn, Pb and Zn in the soil solution near canal water significantly increased with respect to the distance from canal (i. e., 1 m > 5 m). Samples taken near the canal were found more contaminated with metals as compared to the sample away from the canal. It has been reported elsewhere that wastewaters carry appreciable amounts of trace toxic metals [18-22]. Cadmium, Cr and Cu concentrations of soil were directly related to the distance from canal. Soil sampled at 5 m distance contained higher content of these metals as compared to soil sample near canal site. This could be attributed to the nature of soil and the mobility of metals from earthen canal of water.

Table-1: Concentrations of heavy metals (mg L^{-1}) in canal water

Elements	Canal water	NEQ standard*
Cd	0.036	0.1
Cr	3.907	1.0
Cu	0.595	1.0
Fe	15.734	2.0
Mn	22.007	1.5
Pb	6.121	0.5
Zn	2.533	5.0

*National Environmental Quality Standards (NEQS) for the municipal and liquid industrial effluents.

Soil samples exceeded the permissible limits for Zn, Mn, Fe and Cu whereas the Cr and Pb were found within limits, irrespective of the distance from canal. According to the WHO standards (1996), the permissible limits (mg kg^{-1}) of Cr, Cu, Fe, Mn, Pb and Zn in soils are 8, 0.5, 50, 1, 13 and 1.5, respectively. In this experiment, soils accumulated higher amount of Fe and Mn contents whereas the concentration of Cu in the soils was found low as compared to the other elements. Lower concentration of some metals may indicate their lower solubility in soil solution. Manganese is an essential element for plants and its contents in the soils have been reported higher than other microelements except Fe [23]. The critical Mn concentration in the soils is 1500 to 3000 mg kg^{-1} as reported by Kabata-Pendias and Pandias [24]. Whereas the critical concentration in plants ranged from 300 to 500 mg kg^{-1}. Critical level of Cd in soil was reported to be between 3 to 5 mg kg^{-1} [25]. Accumulation of Cd in soil was reported by Yarlagadda [26] and Kachenko and Balwant [27] when irrigated with waste effluents. Alloway [28] reported the most common sources for Cd in the soils and plants are phosphate fertilizers, non-ferrous smelters, Pb and Zn mines, sewage sludge application and combustion of fossil fuels. The concentration of Pb detected was within permissible limit of WHO, i.

e., 13 mg kg^{-1} as reported by Kachenko and Balwant [27] and Ihsanullah *et al.* [29]. Increased quantity of Pb was reported in soil by Miller *et al.* [30]. Yarlagadda *et al.* [26] reported higher Cr in soils near industries. Yarlagadda *et al.* [27] conducted research on the major soil contaminant and found that out of 498 samples of soil 330 had heavy metals as a principal contaminants and Pb, Hg, As, Cr, Cd and Cu were found to be the most commonly occurring metals. Khan [31] reported the impact of industrial effluents on soils and found heavy metals (such as Ni, Zn, Fe, Cu, Pb, Cr and Mn) above permissible limits.

The pH and electrical conductivity (EC) of soils are indicators of the background chemical matrices of the soils and they may be, over the long run, affected by the water quality, organic and inorganic inputs. Samples near wastewater exhibited highest EC value (1.22 dS m^{-1}) whereas the soil samples at 5 m distance exhibited lower EC (0.97). The pH trend was found similar to EC with respect to sampling sites. The pH at 1m distance was found as 7.56 whereas it was recorded as 7.21 at 5m distance. The soil pH and EC levels may have been enhanced due to the seepage of polluted water from earthen canal.

Plant Analysis

Heavy metals concentrations were apparently found dependent on the plant species (Table-2). Vegetations differed for metal concentrations in the order of *A. viridis* > *E. alba* > *H. euoropeum* > *L. nodiflora* > *C. murale* > *C. didymus* > *C. ductylon* > *T. terristris.* Metal concentrations were differed as Fe > Mn > Zn > Pb > Cr > Cu > Cd. These concentrations were associated with plant species. For instance *A. viridis* exhibited higher accumulation of Fe, Cu, Pb and Zn whereas *C. murale* appeared to have higher concentrations of Cu, Pb, Mn and Cr. *T. terristris* got higher Cd and Zn whereas *L. nodiflora* accumulated higher level of Cd. An enhanced level of metals in the soil and cropping system under the influence of industrial effluents has been reported by Khan [31] and Marshal *et al.* [32]. Several aquatic species have the ability to remove heavy metals from water, including water hyacinth (*Eichhornia crassipes* [33, 34], pennywort (*Hydrocotyle umbellata* L. [35] and duckweed (*Lemna minor* L. [36]. There is a consensus that leafy vegetable plants have greater capacity to accumulate heavy metals as compared to other vegetables [27, 31, 32, 37, 38].

Table-2: Concentration of heavy metals (mg kg^{-1}) in natural vegetation collected nearby wastewater canal.

Plant species	Cd	Cr	Cu	Fe	Mn	Pb	Zn
Tribulus terrestris	**0.18**	**0.31**	**0.25**	**0.26**	**5.50**	**0.28**	**2.28**
Lepia nodiflora	**0.11**	**0.39**	**0.18**	**17.68**	**6.10**	**0.41**	**0.86**
Amaranthus viridus	**0.07**	**0.51**	**0.41**	**43.13**	**5.93**	**1.01**	**2.17**
Heliotropium europium	**0.06**	**0.54**	**0.25**	**24.42**	**4.77**	**0.99**	**1.58**
Coronopis didymus	**0.05**	**0.47**	**0.07**	**8.90**	**4.80**	**0.13**	**0.29**
Cynodon ductylon	**0.06**	**0.49**	**0.20**	**3.99**	**3.53**	**0.56**	**1.94**
Chenopodium murale	**0.06**	**0.56**	**0.52**	**8.29**	**6.13**	**1.13**	**0.72**
Eclipta alba	**0.07**	**0.61**	**0.36**	**36.27**	**6.24**	**0.83**	**1.02**
LSD (0.05)	**0.02**	**0.05**	**0.10**	**2.32**	**1.02**	**0.45**	**0.34**

Experimental

Soil Analysis

Soil was sampled at a distance of 1 m and 5 m from the wastewater canal up to a depth of 20 cm. The soil samples were sieved with 2 mm sieve and then air dried. Soil was classified as sandy clay loam by pipette method [17]. The pH and electrical conductivity (EC) of the soil were measured in 1: 5 sample: water suspension after shaking it for one hour by a mechanical shaker. A weighed sample of soil was digested with 25 mL concentrated HCl by gradual heating over a hot water bath for 1 h. After drying, 20% HNO_3 was added to the sample and heated again for 1h. The solution was diluted to 100-mL with distilled water and passed through a 0.22µM filter. Samples were analyzed for heavy metals (Fe, Mn, Zn, Pb, Cr, Cu and Cd) by atomic absorption spectrophotometer.

Plant Analysis

Shoot samples of *Tribilas terristris, Lepia nodiflora, Amaranthus viridis, Heliotropium europeum, Coronopis didymus, Cynodon ductylon*, *Chenopodium murale* and *Eclipta alba* were collected from the sides of earthen wastewater canal (Palosai khwar) near Agricultural University, Peshawar in plastic bags and brought to the laboratory where plants were subjected to shoot analysis. The Palosai canal has been receiving wastewater from houses, industries of Hayatabad Industrial Estate and other non-point sources. Heavy metal contents of wastewater have been reported in our earlier reports (Table-1). Plants shoots were oven dried at 60^{o} C for 48 hours, ground and sieved via 0.05 mm sieve. The powdered samples were transferred to crucible and placed in a muffle furnace at 450 ºC for 2 hour. The crucibles were cooled in desiccators. One gram of ash was taken in 100 mL beaker. Ten mL of conc. HNO_3 was added. The beaker was covered and heated on a hot plate until the material was fully digested. Five mL of concentrated $HClO_4$ was added and then heated at

250 ^{o}C until white fumes appeared. Thereafter, samples were filtered and then diluted up to 100 mL with deionized water. Plant samples were analyzed for heavy metals (Fe, Mn, Zn, Pb, Cr, Cu and Cd) by atomic absorption spectrophotometer. Statistical analysis of data was done using Stat view software [39]. The means of metal contents in plants and soil samples were compared using the Fischer's least significant difference.

Conclusions

It is concluded that sampling areas potentially contaminated with wastewater exhibited higher amounts of heavy metals in both soil and plants. The analyzed species of heavy metals in the soils may reflect the variability of metal composition in the wastewater. Electrical conductivity and pH of the soils and water samples significantly enhanced near earthen canal. Most of the metals in soil were in excess to their permissible limits. Screening plants for metal accumulation would help to find a better option for phytoremediation of wastewaters. The metal hazard in wastewater should be rationalized while applying to the agricultural lands and a comprehensive irrigation management with poor quality water is critical for the protection of environment.

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